

CO and CO₂ emissions from spontaneous heating of coal under different ventilation rates

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ABSTRACT

Carbon monoxide (CO) and carbon dioxide (CO₂) emissions during a spontaneous heating event in a coal mine are important gases to monitor for detecting the spontaneous heating at an early stage. However, in underground coal mines, the CO and CO₂ concentrations and their related fire ratios may be affected by mine ventilation. In this study, CO and CO₂ emissions from spontaneous heating of a U.S. coal sample were evaluated in an isothermal oven under different airflow ventilation rates ranging from 100 to 500 cm³/min. Laboratory experiments were conducted at oven temperatures of 70, 90, and 100 °C. The temperature at the center of the coal sample was continually monitored, while the CO, CO₂, and oxygen (O₂) concentrations of the exit gas were continually measured. The results indicate that CO was generated immediately after the airflow passed through the coal, while CO₂ was generated in a late phase. The amounts of CO generated under different airflow rates were approximately the same at the initial temperature of 70 °C, while the amounts of CO generated increased significantly as the airflow rates and initial temperatures increased. The ratio of CO/CO₂ was found to be independent of airflow rate and initial temperature, approaching a constant value of 0.2 quickly if there was no thermal runaway. The value tended to decrease when a thermal runaway took place. The CO/O₂ deficiency ratio was dependent on both airflow rates and the initial temperature. The experimental results are in qualitative agreement with some large-scale test and field monitoring results.

1. Introduction

Coal mine fires caused by spontaneous heating generally occur by slow oxidation in the coal seams or gob areas and happen most frequently with low-rank coals. Spontaneous heating is a low-temperature coal oxidation reaction which takes place when coal is exposed to air. Coal oxidation is an irreversible exothermic reaction and its reaction rate increases with temperature. When the heat produced by the coal oxidation is not adequately dissipated by conduction or convection, the temperature in the coal mass increases. This increase in temperature leads to an increase in the coal oxidation rate. If not averted with appropriate action, this process results in thermal runaway and a fire ensues.

Spontaneous heating has long been a problem in the mining, storage, and transport of coal. Much research has been done to understand the effects of different parameters on the spontaneous heating process (Akgun and Arisoy, 1994; Beamish and Hamilton, 2005; Carras and Young, 1994; Kucuk et al., 2003; Monazam et al., 1998; Nugroho et al., 2000; Ren et al., 1999; Smith and Glasser, 2005; Smith and Lazzara, 1987; Wang et al., 2003a). The petrographic and geochemical properties of coal waste during self-heating process were

investigated by Misz et al. (2007) and Misz-Kennan and Fabianska (2010). Some works have been done to study the gas emissions from spontaneous combustion of coal and their impact on the environment (Carras et al., 2009; Pone et al., 2007). However, the chemical reaction between coal and O₂ at low temperatures is complex and still not well understood. Generally, three types of processes are believed to occur (Carras and Young, 1994): (i) physical adsorption of O₂; (ii) chemical adsorption which leads to the formation of coal-O₂ complexes and oxygenated carbon compounds; and (iii) oxidation in which the coal and O₂ react with the release of gaseous products, typically CO, CO₂, and water vapor (H₂O).

Although a number of methods have been proposed and used in laboratory experiments in an attempt to predict the spontaneous combustion tendencies of coals, spontaneous heating events still occur in underground coal mines because of complicated parameters such as ventilation airflow, geological conditions, and mining practices that are not considered in laboratory experimental conditions. However, it is well understood that if a spontaneous heating event is detected early enough, some prevention measures can be taken to control and suppress the heating. Therefore, early detection is critical in the prevention and control of fires caused by spontaneous combustion in underground coal mines.

The primary method used for the detection of spontaneous combustion in underground coal mines is the analysis of the gaseous products of coal oxidation using a gas analyzer or a gas chromatograph.

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The gaseous products of low-temperature oxidation at the very early stages are CO, CO₂, and H₂O. Methane (CH₄), hydrogen (H₂), and other low-molecular hydrocarbons are released as the temperature rises. Chamberlain and Hall (1973) found that CO is the most sensitive indicator of the early stages of coal oxidation, and the continuous monitoring of this gas provides the earliest detection of self-heating. Other gases have also been investigated, such as CO₂, CH₄, H₂, and higher hydrocarbons (Xie et al., 2011). CO₂ production increases with increasing temperature and is useful in determining the state of a fire. However, several sources of CO₂ can be present in mines, making its use unreliable. CH₄ is usually present in large background quantities and, as with H₂ and other hydrocarbons, is not produced until much higher temperatures are reached. Since many of the combustion product gases, including CO, are encountered in the normal mining of the coal seam, and because these gas concentrations fluctuate with changes in ventilation, the reliability of these gases as indicators of spontaneous combustion diminishes.

To better detect spontaneous heating in underground coal mines, some fire ratios, such as Graham's ratio (CO/O₂ deficiency) and Trickett's ratio (CO/CO₂) are used. These ratios were originally developed and are often used for assessing the status of a sealed-off fire with the gas samples usually collected behind the seal, as investigated by Singh et al. (2007). The application of fire ratios to detect a spontaneous fire in underground coal mines has had limited success because the gas concentrations are dependent not only upon the state of development of the heating but also upon the mass of coal involved in the heating, airflow flux through the heating zone, and the flow of air into which the gaseous products of the heating are mixed. Different fire ratios have also been used to detect the spontaneous heating at the early stage.

Cliff et al. (2000) conducted large-scale tests for detection and monitoring of spontaneous combustion of coal. They found that the best indicators of spontaneous combustion are those that are independent of airflow, such as the amount of CO released and Graham's ratio, but that even these indicators have some limitations. Chakravorty and Woolf (1979) found that the absolute level of CO in the mine air, whether high or low, is not of great significance but that an increasing trend is indicative of heating. In the U.S., the Graham's ratio (CO/O₂ deficiency) in the mine atmosphere has become the most widely used indicator of the occurrence of spontaneous combustion (Mitchell, 1996).

In this paper, laboratory-scale experiments were conducted to investigate the effect of ventilation on the CO and CO₂ emissions from a spontaneous heating. The influence of ventilation on two commonly used fire ratios is also examined. The experimental results have implications for the early detection of the spontaneous heating in underground coal mines.

2. Experimental

Experiments were conducted in an isothermal oven. The oven temperature can be set from 40 to 200 °C, within an accuracy of ± 0.5 °C. Hereafter, the oven temperature is referred to as the initial temperature. Fig. 1 shows a schematic of the experimental setup. During the test, the coal sample is contained in a brass wire mesh basket, 6-cm-diameter by 10-cm-high, which is enclosed in a brass container. The container has ports in the bottom and top to allow gas to flow through the coal sample. The container is placed at the center of the oven. The ventilation gas (air or nitrogen) is introduced into the container from a compressed gas cylinder. The gas is pre-heated to the oven temperature by passing through heat exchange coils in the oven. Initially, the coal sample is heated to a selected temperature while exposed to a flow of pre-heated nitrogen. The gas flow is then switched to the same flow rate of air.

With air flowing through the coal sample, coal oxidation takes place. Three 0.5-mm-diameter type-K thermocouples are placed at the center of the coal, 3 cm above and below the coal center, respectively, to measure the coal temperatures. The exhaust gas exits the container and travels through a water trap before passing through O₂, CO, and CO₂ gas analyzers. The CO and CO₂ concentrations are measured continuously using an infrared gas analyzer, while the O₂ concentration is measured by a paramagnetic O₂ analyzer. The measurement range is 0 to 5000 ppm for CO, 0 to 10,000 ppm for CO₂, and 0 to 25% for O₂. Tests are terminated when the coal temperature is decreasing or the coal temperature approaches 250 °C.

The coal sample used in the study is a bituminous coal from the western United States. The proximate and ultimate analyses for the coal sample are given in Table 1. To prepare the coal for testing, lumps of fresh coal are first passed through a jaw crusher and then sieved. A 100-gram sample of the 100 × 200 mesh (75 × 150 μm) size fraction is then dried in the oven under nitrogen at 67 °C with a flow rate of 200 cm³/min prior to the experiment.

3. Experimental results and discussion

3.1. Time difference between CO and CO₂ emission onset

Experiments to measure CO and CO₂ emissions were conducted under various ventilation rates at oven temperatures of 70, 90, and 100 °C. Although CO appears at a temperature well below 70 °C for some coals, CO concentrations for this coal at a temperature below 70 °C under the experimental conditions in this study were very low, especially with higher ventilation rates, and the values became unreliable and less repeatable. At 100 °C, this coal experienced a thermal runaway. Therefore, 90 °C was selected as 10 °C below its critical temperature, 100 °C. Fig. 2 shows CO, CO₂, and O₂ concentrations

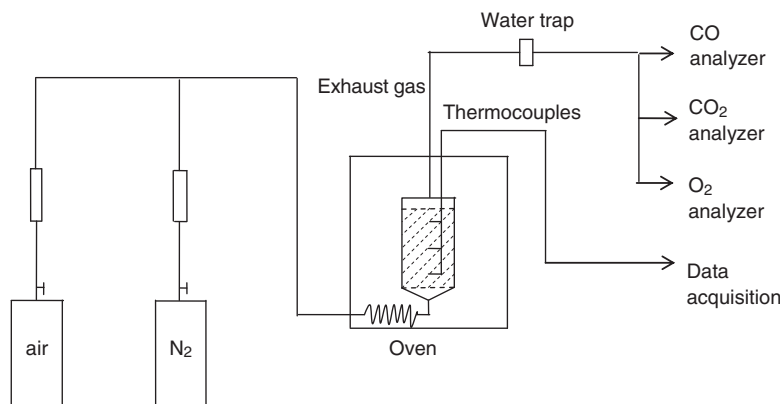


Fig. 1. Schematic of experimental setup and measurement.

Table 1Proximate and ultimate analyses of the coal sample.^a

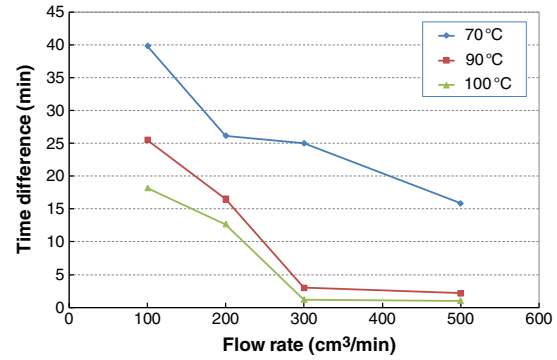
Proximate analysis (%)	Volatile matter	44.0
	Fixed carbon	47.5
	Ash	8.5
Ultimate analysis (%)	Hydrogen	5.5
	Carbon	77.8
	Nitrogen	1.5
	Sulfur	2.6
	Oxygen	12.6

^a Proximate analysis is on dry basis, and the ultimate analysis is on dry ash-free basis.

for the coal sample at an initial temperature of 70 °C with the ventilation rate of 200 cm³/min. Results indicate that the CO was generated earlier than CO₂. The concentrations of both gases increased to a maximum value quickly, then began to decrease. The maximum concentration of CO₂ was about 5 times the concentration of CO. The CO₂ concentration also decreased more rapidly than the CO concentration. In all of the experiments, CO was detected earlier than CO₂. The results indicate that CO was generated immediately after the airflow passed through the coal, while CO₂ was generated in a late phase. This was also observed in other experiments in this study.

Fig. 3 shows the difference in CO and CO₂ emission onset time for tests at the initial temperatures of 70, 90, and 100 °C and flow rates of 100, 200, 300, and 500 cm³/min. These airflow rates were selected to generate a significant spontaneous heating but without a thermal runaway at lower flow rate and a thermal runaway at the higher flow rate based on the experimental conditions and the amount of coal sample used in this study. Experimental results show that the time difference between CO and CO₂ emission onset depends on both the initial temperature and the ventilation rate. At the same initial temperature, the time difference between the CO and CO₂ emission onset decreased with the increasing ventilation rates. The time difference also decreased with the increased temperature at the same ventilation rate. The maximum time difference was 40 min at 70 °C with the flow rate of 100 cm³/min, while the minimum time difference was 1 min at 100 °C with the flow rate of 500 cm³/min.

Figs. 4 and 5 show the CO, CO₂, and O₂ concentrations for the experiments with the flow rate of 200 cm³/min and the initial temperature of 90 and 100 °C, respectively. At 90 °C, the O₂ concentration was 15.6% after the initial phase, while the CO concentration increased to 460 ppm during the same time period. Then, both concentrations increased slowly. At 100 °C, the O₂ concentration was 13.2% after the initial phase, while the CO concentration increased to 950 ppm during the same time period. Then, the O₂ concentration decreased quickly, while the CO concentration increased quickly, indicating that a thermal runaway was occurring. Results indicate that no CO₂ was

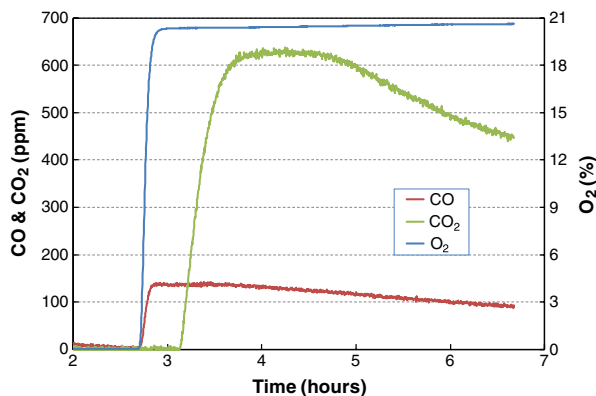
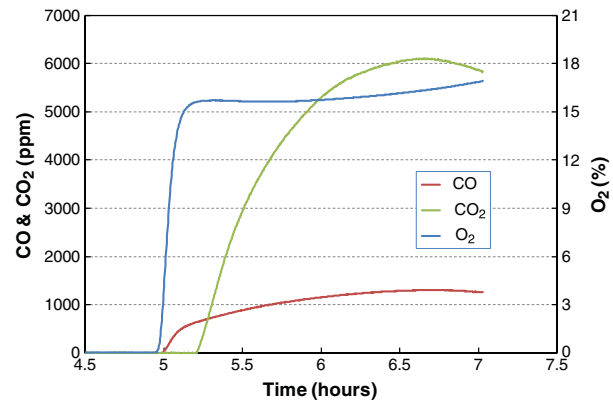
**Fig. 3.** Time difference between CO and CO₂ emission onset.

generated during the initial phase; CO₂ was generated only after the initial phase. As the initial temperature increased from 70 to 90 and 100 °C, the oxidation process started earlier, leading to the smaller time difference between CO and CO₂ emission onset. There are no similar experimental results in the literature for comparison because most gas emission experiments were conducted using a gas chromatography and were not measured continually.

3.2. Effect of ventilation on CO and CO₂ emission rates

If the same amount of a gas is produced at the same initial temperature under different flow rates, the gas concentration at the exit would decrease proportionally with the increase of ventilation rate. To examine the effect of ventilation on the CO and CO₂ gas emission rates, the amounts of gas generated during the heating process were plotted in Figs. 6 and 7 for the coal sample at an initial temperature of 70 °C under different ventilation rates. At 70 °C, the CO and CO₂ emission rate curves for 200, 300, and 500 cm³/min flow rates nearly overlap, indicating a pure dilution effect of the ventilation. Experimental results also show that there is sufficient O₂ available at the lowest airflow rate to sustain the coal oxidation reaction. At 100 cm³/min flow rate, the CO emission rate curve was slightly higher than those at larger ventilation rates, while the CO₂ emission rate curve was lower than those at larger ventilation rates.

The coal sample center temperatures under different ventilation rates are shown in Fig. 8. It is interesting to note that the highest temperature occurred at the flow rate of 100 cm³/min, while the lowest temperature occurred at 200 cm³/min. The ventilation not only provides O₂ for the coal oxidation (heating) but also carries away the heat through convection. Higher ventilation provides more O₂ for the heating, but also carries away more heat. The coal temperature is

**Fig. 2.** CO, CO₂, and O₂ concentrations at initial temperature of 70 °C and ventilation rate of 200 cm³/min.**Fig. 4.** CO, CO₂, and O₂ concentrations at initial temperature of 90 °C and ventilation rate of 200 cm³/min.

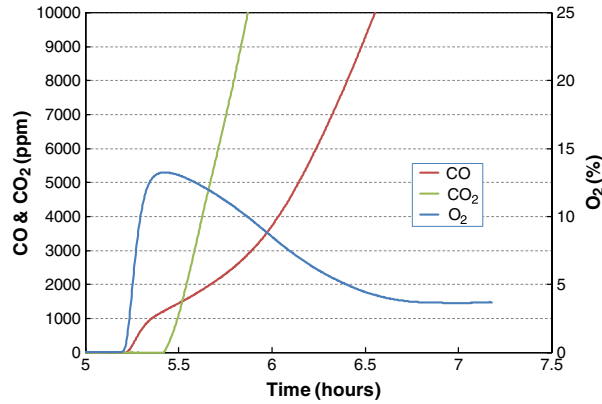


Fig. 5. CO, CO₂, and O₂ concentrations at initial temperature of 100 °C and ventilation rate of 200 cm³/min.

controlled by this combined effect of ventilation on the spontaneous heating.

Figs. 9 and 10 show the CO and CO₂ emission rates for the coal sample at 90 °C initial temperature under different ventilation rates. The gas emission rate curves no longer overlapped, but became distinct. The highest CO and CO₂ emission rates both occurred at the flow rate of 200 cm³/min, while the lowest CO₂ emission rate occurred at the flow rate of 300 cm³/min. The coal sample center temperatures under the different ventilation rates are shown in Fig. 11. At 90 °C initial temperature, the highest temperature also occurred at 200 cm³/min. At this flow rate, enough O₂ was provided for spontaneous heating and not too much heat was lost, leading to the highest temperature. Thus it can be seen that the CO and CO₂ emission rates were following the same pattern as the coal center temperatures under different ventilation rates, implying that coal temperature greatly influences the CO and CO₂ emission rates compared to dilution. Because the rate of coal reaction increases with the temperature exponentially, the CO and CO₂ emission rates increase quickly with the temperature. At both 70 and 90 °C, no thermal runaway was reached, and CO and CO₂ emission rates increased first, then decreased.

Figs. 12 and 13 show the CO and CO₂ emission rates for the coal sample at 100 °C initial temperature under different ventilation rates. The gas emission rate curves became clearly distinct. Both CO and CO₂ emission rates increased with time, eventually beyond the measuring scale. With the increase of ventilation rate, the CO and CO₂ emission rates also increased. At this initial temperature, a thermal runaway was achieved with the flow rate of 200, 300, and 500 cm³/min. The coal sample center temperatures are shown in Fig. 14. With the increase of ventilation rate, the coal temperature also increased. This

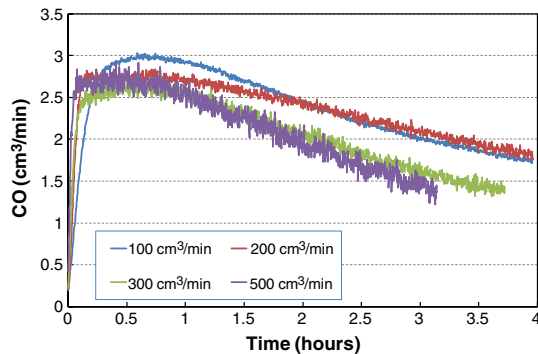


Fig. 6. CO emission rates under different ventilation rates—initial temperature 70 °C.

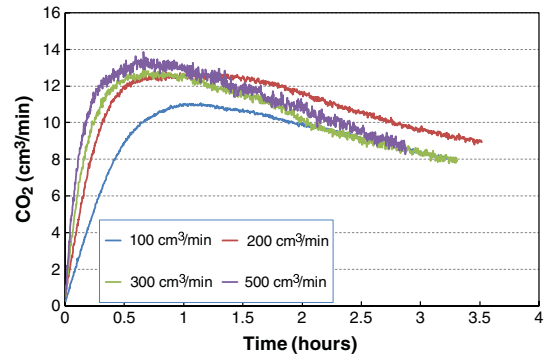


Fig. 7. CO₂ emission rates under different ventilation rates—initial temperature 70 °C.

finding is different from the experimental results at initial temperatures of 70 and 90 °C. This is probably because the heat carried away by ventilation, even at 500 cm³/min, was much less than the heat generated by the coal oxidation at 100 °C initial temperature. As with the initial temperature of 90 °C, the CO and CO₂ emission rates were controlled by the reaction rate, as evidenced by the center temperature of the coal. After the thermal runaway was achieved with the flow rate of 200 cm³/min and above, the CO and CO₂ emission rates increased very quickly. The dilution effect of the ventilation became minimal, and temperature had a major effect on the CO and CO₂ emission rates during the heating process.

3.3. Effect of ventilation on fire ratios

Fire ratios have been used for the purpose of early detection of spontaneous heating. Results indicate that the CO and CO₂ concentration are affected by the ventilation in situations where thermal runaway has not occurred. Once a condition of thermal runaway occurs, the emission rate is reaction rate controlled. Therefore, fire ratios are more important in early detection since thermal runaway has not occurred. For the coal sample used in this study, and because the CO was always generated earlier than the CO₂, the CO/CO₂ ratio and the CO/O₂ deficiency ratio are the potential ratios to use in mine applications. Figs. 15, 16, and 17 show the CO/CO₂ ratios under different ventilation rates at the initial temperatures of 70, 90, and 100 °C, respectively. During the test, the CO₂ concentration increased beyond the CO value very quickly after CO₂ was detected. The CO/CO₂ ratio was initially high, then decreased quickly to the value of 1. Therefore, the CO/CO₂ ratio was plotted starting from the value of 1. The ratios under different ventilation rates decreased very quickly and leveled off around the value of 0.2 at the initial temperatures of 70 and 90 °C as shown in Figs. 15 and 16. These results imply that the ventilation rate and initial temperature have little effect on the CO/CO₂

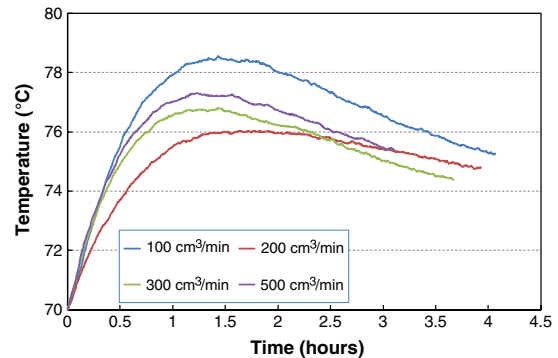


Fig. 8. Coal center temperatures under different ventilation rates—initial temperature: 70 °C.

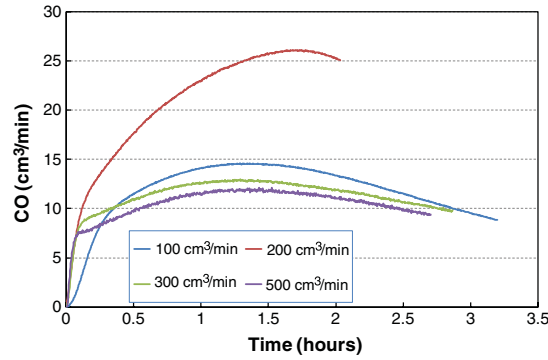


Fig. 9. CO emission rates under different ventilation rates—initial temperature 90 °C.

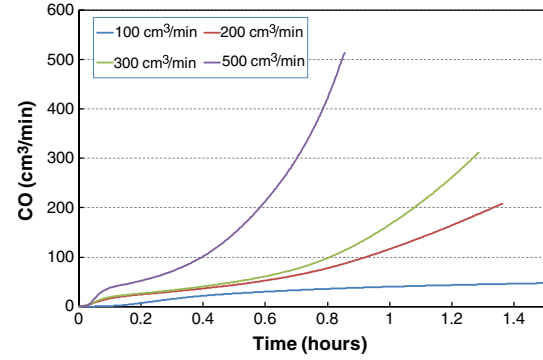


Fig. 12. CO emission rates under different ventilation rates—initial temperature 100 °C.

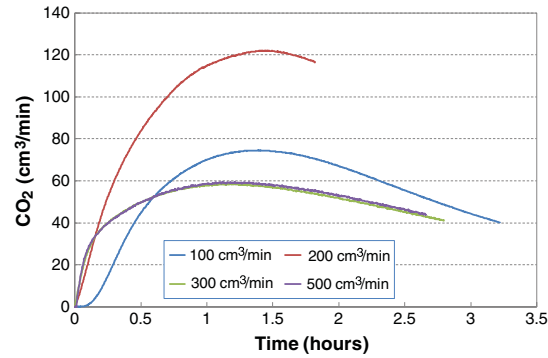


Fig. 10. CO₂ emission rates under different ventilation rates—initial temperature: 90 °C.

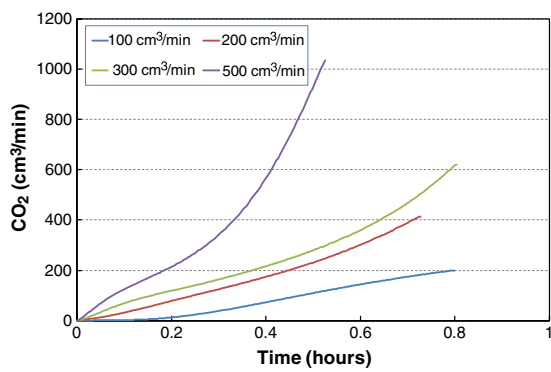


Fig. 13. CO₂ emission rates under different ventilation rates—initial temperature 100 °C.

ratio when there is no thermal runaway occurring. It should be noted that the CO/CO₂ ratio decreased quickly even as the coal temperature continually increased.

Although the CO/CO₂ ratio values under different ventilation rates also decreased at the 100 °C initial temperature, the ratios did not level off around the value of 0.2 but instead decreased continually below 0.2. Because of the limitation of the gas monitor, not many data points below the value of 0.2 were obtained. However, the trend of the data indicates that when the thermal runaway took place, the ratio tended to decrease quickly below the value of 0.2. This is consistent with field monitoring results from Timko and Derick (1995), predicting spontaneous heating in underground coal mine pillars. In their study, several boreholes were drilled into pillars. Each hole was 3.8 cm in diameter. These holes were aligned at right angles to the coal cleat and drilled horizontally. A 0.95-cm outside diameter gas sampling line stopped just inside the borehole opening. The end of each hole was sealed with a urethane foam plug.

The gas data were analyzed by a gas chromatograph. The CO data gradually increased—an indication of accelerating oxidation. However, the CO/CO₂ ratio remained essentially unchanged until the fire occurred. This unchanged value was about 0.08, and the ratio value decreased quickly as the thermal runaway took place.

In a large-scale spontaneous combustion experiment conducted by Smith et al. (1991), similar results were obtained. In their experiment, approximately 11,800 kg of Wyoming No. 80 seam coal was tested in a 1.8-m-high by 1.8-m-wide by 4.5-m-long coalbed chamber. Initially, a 50-L/min airflow was established. O₂ concentrations quickly fell to less than 2% in the center of the coalbed and to 15% near the front of the coalbed. Meanwhile, temperatures rose steadily over the entire coalbed. Corresponding increases in CO across the coalbed ranged from 0.1% to 0.3% while CO₂ was near the detection limit, indicating

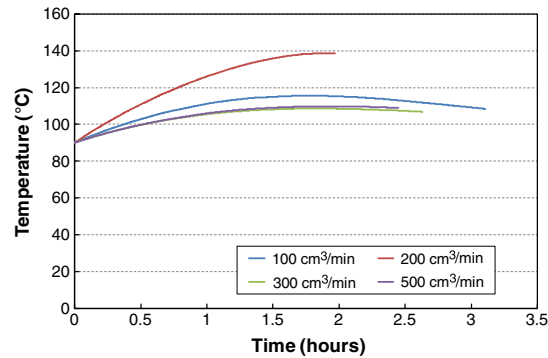


Fig. 11. Coal center temperatures under different ventilation rates—initial temperature 90 °C.

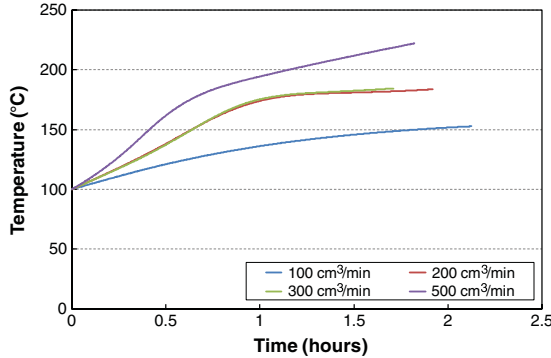


Fig. 14. Coal center temperatures under different ventilation rates—initial temperature 100 °C.

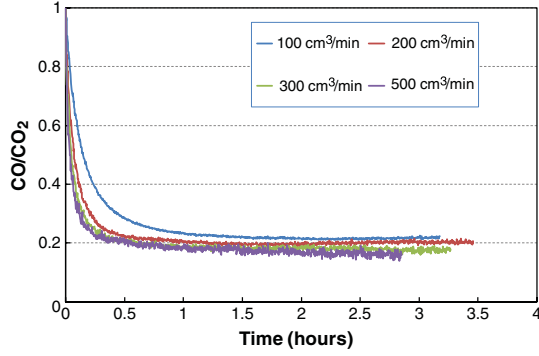


Fig. 15. CO/CO₂ ratio under different ventilation rates—initial temperature 70 °C.

CO generation from the O₂ adsorption. At day 7.6, the airflow was increased to 150 L/min. Temperatures continued to rise, O₂ concentrations continued to decrease, and a slight increase in the CO₂ concentration was observed. CO concentrations were stable or slightly decreasing, indicating the onset of coal oxidation. The CO/CO₂ ratio in the experiment was 0.25 at day 21.7 and 0.22 at day 25. This is qualitatively consistent with the results in this study.

Wang et al. (2002, 2003b) conducted experiments to examine CO, CO₂, and H₂O formation during low-temperature oxidation of an Australian bituminous coal. At temperatures between 60 and 90 °C, they found that the most important carbon-containing gaseous product of oxidation is CO₂. CO is emitted in smaller amounts, with a molar ratio of CO₂/CO production of about 3. They also found that the ratio of the rates of production of CO₂ and CO has a rather high value at the beginning of the experiment, but decreases with time, and that the ratio evidently depends on temperature. This finding is contradictory to the result in this study, probably because of different coal properties.

Figs. 18, 19, and 20 show the CO/O₂ deficiency ratio under different ventilation rates at the initial temperatures of 70, 90, and 100 °C, respectively. Results indicate that the ratio was strongly affected by the ventilation and the initial temperature. At 70 °C, the ratio tended to be leveled off at the 100 and 200 cm³/min flow rates after its initial rise, while it increased quickly at the 300 and 500 cm³/min flow rates. At 90 °C, the ratio increased slowly at the 100, 200, and 300 cm³/min flow rates, while it rose faster at the 500 cm³/min flow rate. At 100 °C, the ratio increased very rapidly except at the 100 cm³/min flow rate. These results imply that the CO/O₂ deficiency ratio changed very little at the lower initial temperature and the lower ventilation rate. However, with the higher ventilation rate, this ratio rose even at the lower initial temperature. When thermal runaway was reached, the ratio rose quickly. In the Timko and Derick (1995) field study, the CO/O₂ deficiency ratio was unchanged (around 0.01) until the fire occurred. This finding is

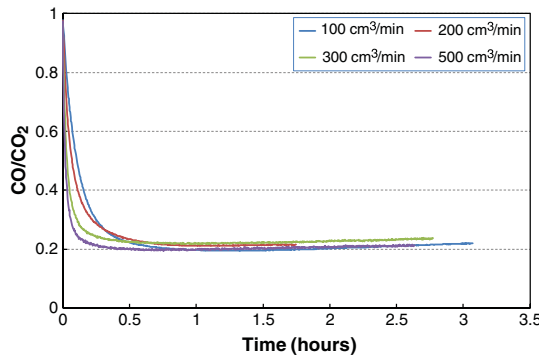


Fig. 16. CO/CO₂ ratio under different ventilation rates—initial temperature 90 °C.

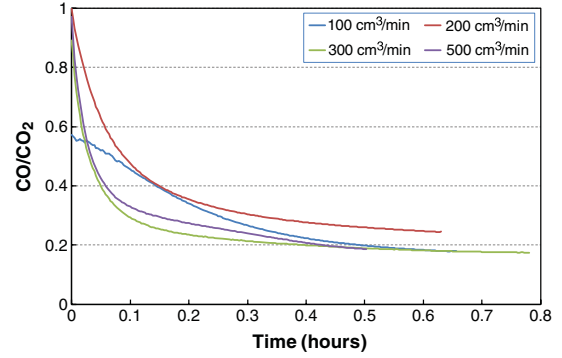


Fig. 17. CO/CO₂ ratio under different ventilation rates—initial temperature 100 °C.

qualitatively consistent with the experimental results in this study, showing the lower ventilation rate at the lower initial temperature.

4. Conclusions

Laboratory-scale experiments were conducted to investigate the effect of ventilation on the CO and CO₂ emission during the spontaneous heating process of a U.S. coal sample. The experimental results indicate that CO was generated immediately after the airflow passed through the coal, while CO₂ was generated in a late phase under the experimental conditions. The time difference between CO

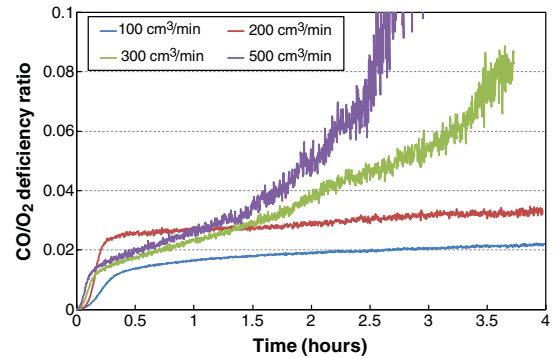


Fig. 18. CO/O₂ deficiency ratio under different ventilation rates—initial temperature 70 °C.

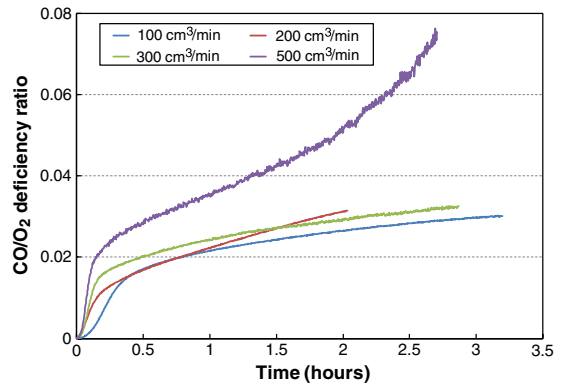


Fig. 19. CO/O₂ deficiency ratio under different ventilation rates—initial temperature: 90 °C.

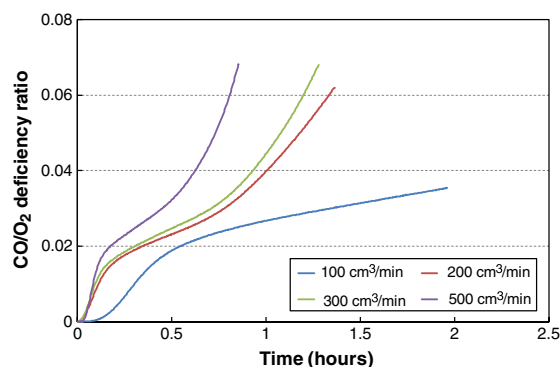


Fig. 20. CO/O₂ deficiency ratio under different ventilation rates—initial temperature: 100 °C.

and CO₂ emission onset decreased with the increase of the initial temperature or the ventilation rate.

At low initial temperature, the ventilation had a pure dilution effect on the CO and CO₂ emission rates. At high initial temperature, the dilution effect from ventilation became insignificant for CO and CO₂ emission rates, and these emission rates became dominated by the reaction rate. Without a thermal runaway occurring, there was an optimum ventilation rate for the highest CO and CO₂ emission rates. With a thermal runaway, the CO and CO₂ emission rates increased with the increase of ventilation rate.

The CO/CO₂ ratio was found to be unaffected by the initial temperature and the ventilation flow rate, leveling off around the value of 0.2 in this study when no thermal runaway occurred. When a thermal runaway occurred, the value of the ratio continually decreased below 0.2. The CO/O₂ deficiency ratio was significantly affected by the ventilation rate except at low initial temperature and low ventilation flow rate.

The results from this study indicate that it is helpful to monitor CO/CO₂ ratio in addition to monitoring CO and CO₂ concentration to detect and prevent spontaneous heating of this particular coal in underground coal mines. It should be noted that the value of the CO/CO₂ ratio indicating thermal runaway is dependent on the coal type. Finally, in case of significant ventilation rate changes, the CO/O₂ deficiency ratio may become unreliable.

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Disclaimer: The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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